Prediction of Specific Volume and Refractive Index of Nondilute Polymer Solutions (Commemoration Issue Dedicated to Professor Hisashi Odani On the Occasion of His Retirement)

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Note

Prediction of Specific Volume and Refractive Index of Nondilute Polymer Solutions*

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van Laar-Scatchard-type equations representing the specific volume and refractive index of nondilute multicomponent solutions were proposed. They were shown to describe experimental data on polymer / solvent binary solutions with sufficient accuracy.

KEYWORDS: Partial specific volume / Refractive index increment / Concentration dependence / Multicomponent polymer solutions / van Laar-type equations

INTRODUCTION

The partial specific volume and refractive index increment of a polymer solution generally exhibit dependence on the solution composition, the details of which are still unknown. Accordingly, studies of concentrated polymer solutions by, e.g., ultracentrifugation and light scattering[1-4] require direct measurements of these quantities over the relevant range of composition, which is quite a laborious task. As the number of components increases, direct measurements become more and more impractical. Need is apparent for some simple, yet sufficiently accurate, treatments.

Here we propose a simple treatment based on the van Laar-Scatchard-type equation of mixing,[5] which has proved useful to treat multicomponent solutions, at least in the dilute limit of polymer concentration(s).[6-8] According to the present extension of this treatment to nondilute solutions, the specific volume and refractivity of a solution of arbitrary composition are readily calculable provided that the physical parameters of the pure components and the infinitely dilute solution be known. The validity of the proposed equations will be checked against some published experimental data on binary solutions.

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2. THEORETICAL

Changes in volume and polarizability upon mixing could be viewed as perturbations caused by contacts of unlike molecules.[6] From this standpoint, we assume that the molar volume V and molar refractivity R (in a monomeric unit basis, for polymers) of a mixing are given in the following forms:

$$V = V^* + V^* \sum_{i<j}\sum a_{ij}\phi_i\phi_j \tag{1}$$

$$R = R^* + V^* \sum_{i<j}\sum b_{ij}\phi_i\phi_j \tag{2}$$

with

$$V^* = \sum_i f_i V_i \tag{3}$$

$$R^* = \sum_i f_i R_i \tag{4}$$

$$\phi_i = f_i V_i / V^* \tag{5}$$

Here f_i, V_i and R_i are the mole fraction, molar volume and molar refractivity of component i ($i = 1, 2, \cdots, n$) with the summations extending over all n components. Clearly, V^* and R^* refer to an ideal mixture and ϕ_i is the volume fraction *before* mixture. The parameters a_{ij} and b_{ij}, which characterize i-j two-body interactions, generally are a function of composition but assumed here to be constants. The molar refractivity R and R_i are defined by

$$R = PV \tag{6}$$

$$R_i = P_i V_i \tag{7}$$

where P and P_i are the polarizabilities of the mixture and pure i, respectively. Equations 2, 6 and 7 give

$$P = [\sum_i \phi_i P_i + \sum_{i<j}\sum b_{ij}\phi_i\phi_j] / [1 + \sum_{i<j}\sum a_{ij}\phi_i\phi_j] \tag{8}$$

The partial specific volume $\bar{v}_i$ of component i is readily obtained from eq. (1)

$$\bar{v}_i = v_i (1 + \sum_{j(\neq i)} a_{ij}\phi_j - \sum_{i<m}\sum a_{jm}\phi_j\phi_m) \tag{9}$$

where v_i is the specific volume of pure i.

For a solvent(1) / polymer(2) binary solution, eq. (8) simply reads

$$\begin{aligned}\bar{v}_2 &= v_2 (1 + a_{12}\phi_1^2) \\ &= v_2 + (\bar{v}_2^0 - v_2)\phi_1^2\end{aligned} \tag{10}$$

with $\phi_1 + \phi_2 = 1$ and $\bar{v}_2^{\circ}$ denoting the partial specific volume in the dilute limit. The apparent specific volume $\bar{v}_2^{app}$ defined by

$$v = w_i v_i + w_2 \bar{v}_2^{app} \tag{11}$$

can be given by

$$\bar{v}_2^{app} = \bar{v}_2^{\circ} + (v_2 - \bar{v}_2^{\circ})\phi_2 \tag{12}$$

In eq. (11), v is the specific volume of the solution, and w ($= 1 - w_2$) denotes the weight fraction :

$$v = \sum_i w_i v_i \tag{13}$$

$$\phi_i = w_i v_i / v \tag{14}$$

The refractive index increment of component i, $\partial n/\partial \phi_i$, can be derived from eq. (8), if the relation between P and refractive index n is known (see below). For the time being, it suffices to assume that P is a function of n only. For, e.g., a solvent(1) / polymer(2) binary mixture, there is obtained

$$\left(\frac{dP}{dn}\right)\left(\frac{\partial n}{\partial \phi_2}\right) = \frac{P_2 - P_1 + a_{12}(\phi_2^2 P_2 - \phi_1^2 P_1) - b_{12}(\phi_2 - \phi_1)}{(1 + a_{12}\phi_1\phi_2)^2} \tag{15}$$

For the sake of convenience, we rewrite eq. (15) in terms of weight fraction w_i and expand the equation around $w_2 = 0$, yielding

$$\partial n/\partial w_2 = \psi_2 + \psi_{22} w_2 + \cdots \tag{16}$$

$$\psi_2 = (v_2 / P_1' v_1)\,[P_2 + b_{12} - P_1\,(1 + a_{12})] \tag{17}$$

$$\psi_{22} = (2v_2^2 / v_1^2 P_1')\,(P_2 - P_1) - (2/v_1)\,(v_2 + \bar{v}_2^{\circ} - v_1)\psi_2 - (P_1''/P_1')\psi_2^2 \tag{18}$$

with

$$P_1' = dP_1/dn_1 \quad \text{and} \quad P_1'' = d^2P_1/dn_1^2 \tag{19}$$

Hence ψ_{22} can be known as a function of ψ_2, $\bar{v}_2^{\circ}$ and other physical parameters of pure components.

3. COMPARISON WITH EXPERIMENTS

Equations 10, 12 and 16 predict $\bar{v}_2$, $\bar{v}_2^{app}$ and $\partial n/\partial w_2$ of binary solutions in terms of the properties of the pure components and those of the infinitely dilute solutions. In order to check these equations against experimental data, we need know the values of specific volume v_2 and the refractive index n_2 of pure polymers at the relevant temperatures. Here we take polystyrene (PS) and poly(methyl methacrylate)(PMMA) as model polymers. Both of these polymers are glasses below about 100°C, and it would be incorrect to adopt the physical constants of the glasses to the discussion of solutions. Hence we will use the values of v_2 and n_2 obtained by extrapolating the liquid polymer data available in the literature (refs. 9 and 10 for v_2 of PS and PMMA, respectively and refs. 11 and 12 for n_2 of PS and PMMA, respectively). Whenever necessary, the wave-length correction was made by use of the Caucy dispersion equation.

Figure 1 compares the experimental values of $\bar{v}_2^{app}$ (circles) and those calculated with eq. (12) (solid lines) for PS and PMMA in bromobenzene[4] and in 2-butane.[13] Figure 2 shows a similar comparison between theory (solid curves) and experiment (broken curves) for PS in toluene at several temperatures. The experimental curves were drawn on the basis of the data reported by Scholte.[1] In all cases, agreement of theory and experiment appears satisfactory.

Known equations between P and n include those of Lorentz-Lorentz (L-L), Eykman (E) and Gladstone-Dale (G-D).[14]

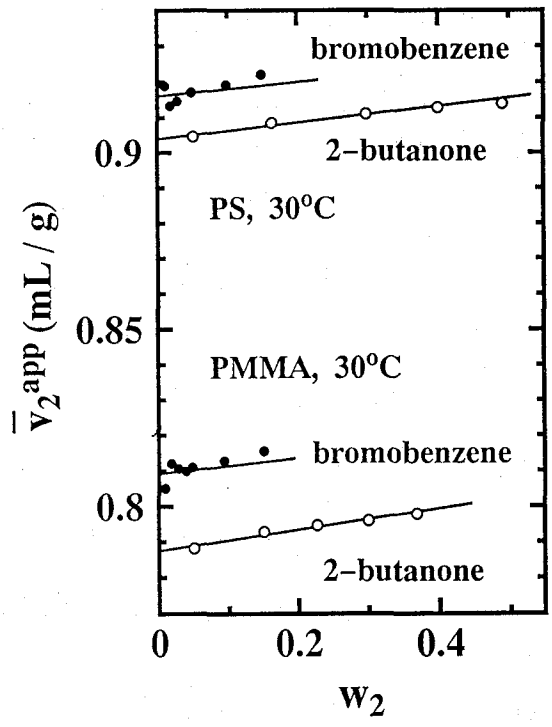

Fig. 1. Comparison of experimental (circles)[4] and predicted (solid curves) values of $\bar{v}_2^{app}$.

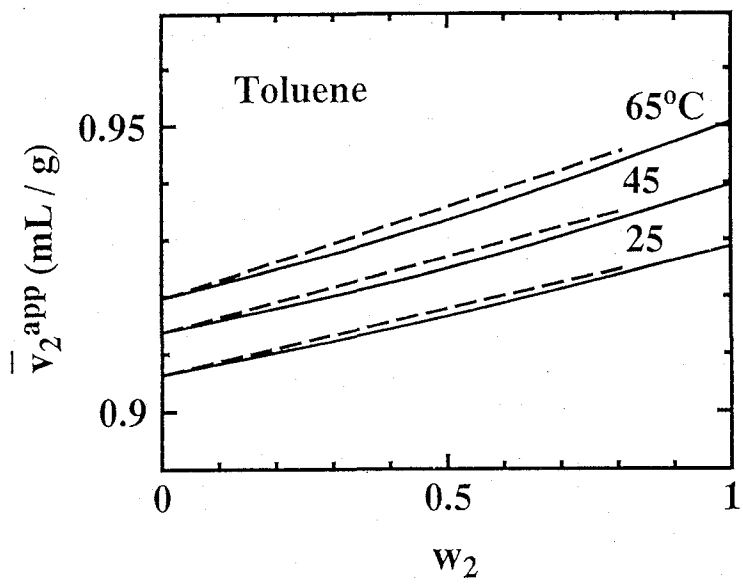

Fig. 2. Comparison of experimental (broken curves)[1] and predicted (solid curves) values of $\bar{v}_2^{app}$.

$$P = (n^2 - 1) / (n^2 + 2) \qquad \text{(L-L)} \qquad (20)$$

$$P = (n^2 + 1) / (n^2 + 0.4) \qquad \text{(E)} \qquad (21)$$

$$P = n - 1 \qquad \text{(G-D)} \qquad (22)$$

In order to test validity of these equations, we have examined refractive index data for about 200 common organic solvents[15]: to do this, we recast eq. (6) as

$$P = \rho r \qquad (23)$$

with ρ and r being the density and the specific refractivity. Since r can be regarded as a constant independent of ρ, eq. (23) gives

$$\rho(\partial n/\partial \rho) = P\,(\partial P/\partial n)^{-1} \qquad (24)$$

The quantity on the left-hand-side of eq. (24) is plotted against n in Figure 3. Since the individual data points are rather scattered, solvents that have similar n were appropriately grouped and an average was taken in each group, for the sake of easy recognition. The curves in the figure show the quantity on the right-hand-side of eq. (24) computed with eqs. (20), (21) and (22). Clearly, the E and G-D equations equally well represent the experimental data, while the L-L equation gives the poorest representation. For this reason,

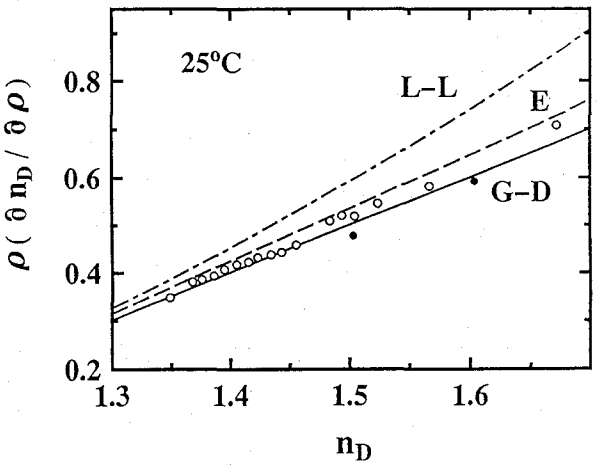

Fig. 3. Plot of ρ $(\partial n_D/\partial \rho)$ vs. n_D for common organic solvents. Each circle represents a mean value over ca. 10 (on average) organic solvents having a similar refractive index n_D for the sodium D line, and the curves represent the Lorentz-Lorentz (L-L), Eykman (E) and Gladstone-Dale (G-D) equations.

we will adopt the G-D equation, the simplest of all. The results do not seriously depend on the *p-n* relation, however.

Table 1 compares the calculated and observed ϕ_{22} values for the toluene/PS[1], cyclohexane/PS[1], decalin/PS[16], bromobenzene/PS[4] and bromobenzene/PMMA[4] systems. Again, satisfactory agreement can be observed in all cases.

Table 1. Comparison of Calculative and Experimental Values of ϕ_{22}[a]

System	Temp. (°C)	Wave L. (nm)	$\bar{v}_2^0$ (mL/g)	ϕ_2	ϕ_{22}^{cai}	ϕ_{22}^{exp}	refs.
PS/TOL	25	546	0.9188	0.0952	0.031	0.0371	1
	45	546	0.9262	0.0992	0.032	0.0374	1
	65	546	0.9330	0.1031	0.036	0.0379	1
PS/CH	30	546	0.9250	0.130	0.072	0.070	1
	45	546	0.9353	0.133	0.073	0.070	1
	65	546	0.9492	0.137	0.073	0.070	1
PS/DCL	20	546	0.9259	0.1099	0.047	0.068	14
	25	546	0.9284	0.1105	0.046	0.054	14
	30	546	0.9309	0.1108	0.047	0.058	14
	40	546	0.9359	0.1110	0.048	0.058	14
PS/BB	30	436	0.9160	0.0711	− 0.063	− 0.073	4
PMMA/BB	30	436	0.8095	− 0.0733	0.009	− 0.009	4

[a]TOL=toluene, CH=cyclohexane, DCL=decalin, BB=bromobenzene.

To summarize, the proposed treatment allows the prediction of the partial specific volume and refractive index increment of nondilute polymer solutions with sufficient accuracy on the basis of the dilute solution data along with the physical constants of pure components. It has been reported[16] that the partial specific volume of PS in *trans*-decalin slightly decreases with increasing polymer concentration (in the relatively low concentration region). Such (perhaps exceptional) behavior cannot be predicted by the present treatment.

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